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ENGINEERING DATA TRANSMITTAL

Page 1 of

1. EDT 604351

2. To: (Receiving Organization)	3. From: (Originating Organization)	4. Related EDT No.:
Waste Tank Characterization (7R000)	Waste Tank Safety Program (7R230)	N/A
5. Proj./Prog./Dept./Div.:	6. Cog. Engr.:	7. Purchase Order No.:
Tank Vapor Issue Program	JL Huckaby	N/A
8. Originator Remarks: The purpose of this Data Quality Objective is to define the information/data needs required to support programmatic decisions regarding the resolution of tank vapor issues relative to generic tanks.		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: Generic Tanks
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1	WHC-SD-WM-DQO-002	All	0	Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution.	SQ	1,2	2	6

MAY 1995 RECEIVED EDMC

16. KEY

Impact Level (F)	Reason for Transmittal (G)	Disposition (H) & (I)
1, 2, 3, or 4 (see MRP 5.43)	1. Approval 4. Review 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)	1. Approved 4. Reviewed no/comment 2. Approved w/comment 5. Reviewed w/comment 3. Disapproved w/comment 6. Receipt acknowledged

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1	1	Cog.Eng.: JW Osborne 3-1-94 R2-78	Env.		
1	2	QA: DC Board 3/3/94 S1-57			
1	1	Safety: ER Hewitt 3/1/94 R3-01			
		Cog. Mgr. SEE Block 20			

18.	19.	20.	21. DOE APPROVAL (if required) Ltr. No.
JW Osborne 3-1-94 Signature of EDT Originator / Date	C DeFigh-Price 3/3/94 Authorized Representative for Receiving Organization / Date	MA Payne 3/3/94 Cognizant/Project Engineer's Manager / Date	[] Approved [] Approved w/comments [] Disapproved w/comments

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Date Received
3-16-94

INFORMATION RELEASE REQUEST

Reference:
WHC-CM-3-4

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- ☑ Other SD

ID Number (include revision, volume, etc.)
SD-WM-DQO-002 Rev 0

List attachments.

Date Release Required 3-21-94

Title: Data Quality Objectives for [illegible]

Unclassified Category: UC-

Impact Level:

New or novel (patentable) subject matter? ☑ No ☐ Yes
If "Yes", has disclosure been submitted by WHC or other company?
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Will proceedings be published? ☐ Yes ☐ No
Will material be handed out? ☐ Yes ☐ No

Title of Journal

CHECKLIST FOR SIGNATORIES

Review Required per WHC-CM-3-4	Yes	No	Reviewer - Signature Indicates Approval: Name (printed)	Signature	Date
Classification/Unclassified Controlled Nuclear Information	☐	☑			
Patent-General Counsel	☑	☐	S.P. Berglin	S.P. Berglin	3/19/94
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Applied Technology/Export Controlled Information or International Program	☐	☑			
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Information conforms to all applicable requirements. The above information is certified to be correct.

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References Available to Intended Audience	☐ N/A	☐
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Author/Requestor (Printed/Signature) — Date: 3-16-94

Intended Audience
☐ Internal ☐ Sponsor ☑ External

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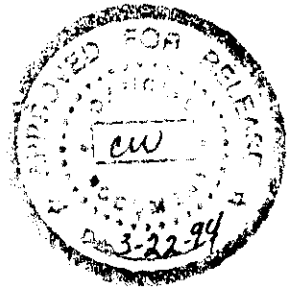

Date Cancelled

Date Disapproved

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SUPPORTING DOCUMENT

1. Total Pages 34

2. Title	3. Number	4. Rev No.
Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution	WHC-SD-WM-DQO-002 Rev. 0	0

5. Key Words	6. Author
Data Quality Objectives/Decision Rules/Signature Characterization/Adaptive Analysis Strategy	Name: J. W. Osborne Signature J W Osborne Organization/Charge Code 7R230/N2110

7. Abstract

The document describes the Data Quality Objectives developed for the generic problem of tank vapor characterization.

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10. RELEASE STAMP

APPROVED FOR RELEASE 3-22-94

OFFICIAL RELEASE BY WHC 5

DATE MAR 07 1994

9. Impact Level SQ

DATA QUALITY OBJECTIVES FOR GENERIC IN-TANK HEALTH AND SAFETY VAPOR ISSUE RESOLUTION

March 1994

Westinghouse Hanford Company

J. W. Osborne
J. L. Huckaby
E. R. Hewitt

Pacific Northwest Laboratory

C. M. Anderson
D. D. Mahlum
B. A. Pulsipher
J. Y. Young

TABLE OF CONTENTS

LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
CES	Consensus Exposure Standard
CGM	Combustible Gas Meter
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy - Richland Operations Office
DQO	Data Quality Objectives
ISS	In Situ Sampling
LFL	Lower Flammability Limit
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
OVS	OSHA Versatile Sampler
PEL	Permissible Exposure Limit
REL	Recommended Exposure Limit
SUMMA®	Registered Trademark for Passivated Stainless Steel Canister
TLV	Threshold Limit Value
TRP	Toxicology Review Panel
USEPA	U. S. Environmental Protection Agency
VSS	Vapor Sampling System
WEEL	Workplace Environmental Exposure Level
WHC	Westinghouse Hanford Company
WDOE	Washington State Department of Ecology

DATA QUALITY OBJECTIVES FOR GENERIC TANK VAPOR ISSUE RESOLUTION

EXECUTIVE SUMMARY

Data Quality Objectives (DQOs) for generic tank vapor and gas sampling were developed in a series of four facilitated meetings and one stakeholder review session, using the most recent U. S. Environmental Protection Agency (USEPA) DQO guidelines. These meetings elicited DQOs for two major vapor problem areas: flammability and toxicity. What follows is a summary of the outputs of the planning team for each of the seven steps of the DQO process. More details regarding the rationale for each of the DQO planning outputs are contained in the DQO document that follows this summary.

Step 1. Problem Statement

Two problems were: 1) potential flammability of gases and vapors in waste storage tanks and 2) potential worker health and safety hazards associated with the toxicity of constituents in any fugitive vapor emissions from these tanks. Previous work reports the presence of a fog in some tanks, and the fuel content of the tank gases and vapors may be too high to permit work in these tanks. Numerous reports of adverse health effects associated with vapor exposures in and around tank farms have been made by workers. Confirmed symptoms from these exposure incidents include headaches, burning sensations in nose and throat, nausea, and impaired pulmonary function.

Data are needed to identify and quantify constituents of the tank headspaces to address potential vapor toxicity. If any compounds of toxicological interest are identified in the tank headspace, industrial hygienists can use this information to assess "worst-case" worker exposure levels and focus their industrial hygiene monitoring strategy on these target compounds. Final recommendations on the required level of personal protective equipment will be based on the worker breathing zone levels of these chemicals. The ultimate goal is to provide a safe and healthful workplace in the tank farms complex.

Resolution of these problems involves a sequence of sampling events. The first sampling event assesses flammability of the volatile organic vapor, ammonia, methane, and other flammable gases present in the tank headspace. If the flammability assessment results are acceptable then special vapor sampling equipment will be installed in the tank. This equipment will be used in subsequent sampling events to: 1) establish concentrations of all flammable headspace constituents; 2) identify compounds of toxicological concern; and 3) quantify compounds of toxicological concern.

Step 2. Decision Statements

A. Flammability Decision

If the total fuel content of the headspace is ≥ 20 % of the lower flammability limit (LFL), then work must stop until further authorization is given by management.

B. Toxicity Decision

If any compounds with toxicological properties exceed their recommended levels inside the tank headspace, then advise Health and Safety. Guideline levels are:

- 10% of the appropriate Consensus Exposure Standard (CES)* concentration for known or suspected human carcinogens, teratogens and mutagens
- 50% of the appropriate CES concentration for non-carcinogens, non-teratogens and non-mutagens, or simple irritants.

Step 3. Inputs to the Decision

- Identification and quantification of flammable constituents in the headspace
- Temperature of the headspace
- Identification and quantification of compounds of toxicological importance
- Understanding of the toxicological effects of these compounds and the CES for each constituent of concern.

Step 4. Boundaries of the Study

The spatial boundaries of the vapor and gas sampling events are defined by the waste surface, walls and dome of the waste tank itself. Sampling events will be scheduled to address diurnal, seasonal, and long-term changes in the vapor and gas concentrations.

* See 3.2 second paragraph for definition

Step 5. Decision Rules

A. Flammability Decision Rule

If the total fuel content of the headspace equals or exceeds 20% of the LFL for the observed mixture, then stop work and take appropriate actions before resuming sampling or other work on the tank.

B. Toxicity Decision Rule

The DQO team established decision rules organizing potentially toxic substances by type to include carcinogens, teratogens and mutagens, systemic toxins, and irritants. The toxicity decision rules were specified as follows:

- If the average concentration of any confirmed or suspected human carcinogen, teratogen, or mutagen in a tank headspace is greater than one-tenth of its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

- If the average concentration of any systemic toxin in a tank headspace is greater than one-half its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

- If the average concentration of any irritants in a tank headspace is greater than one-half of its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

Step 6. Limits on Decision Errors

A. Flammability Decision Errors

One type of decision error would occur if data incorrectly indicate $LFL_{MIX} \geq 20\%$.

A second kind of decision error would occur if data incorrectly indicate $LFL_{MIX} < 20\%$.

B. Toxicity Decision Errors

One type of decision error would occur if data incorrectly indicate that the prescribed toxicity limits have been exceeded, when in fact they haven't.

A second type of decision error would occur if data incorrectly indicate that the prescribed toxicity limits have not been exceeded, when in fact they have.

The relative consequence of the second type of decision error (failure to find a true problem) was determined to be roughly 2.5 times greater than the other type of decision error.

Step 7. Develop and Optimize the Design for Collecting Data

The Westinghouse Hanford Company (WHC) strategy to resolve the flammability and toxicity issues was approved by the U.S. Department of Energy (DOE) reviewers prior to initiation of this DQO (Gerton, O'Dell 1992). The DQO process was consequently limited by constraints imposed by these designs. Therefore, Step 7 addresses the expected performance of the flammability assessment sampling, and the proposed sampling strategy for determining headspace vapor and gas toxicity

* * *

In conclusion, the DQO process for generic vapor sampling has been an examination of the strategy used to generate the data needed to adequately characterize the headspace of these tanks. It has proven beneficial because it has offered the stakeholders an opportunity to assess the goals and objectives of the experimental design and comment on the adequacy of the data to support their need. This re-affirmation of the "correctness" of the approach and ultimate data output enhances overall confidence in the data and ultimately in the safety decisions made from these data.

DATA QUALITY OBJECTIVES FOR GENERIC TANK VAPOR ISSUE RESOLUTION

1.0 INTRODUCTION

This document describes the Data Quality Objectives developed for the generic problem of tank vapor characterization. The DQO and sampling and analysis plan previously developed for the pilot tank vapor sampling effort in tank 241-C-103 (known hereafter as C-103) (Osborne 1992) were heavily relied upon for this generic vapor planning effort. The pilot DQOs and vapor sampling and analysis plan were developed prior to these generic vapor DQOs for several reasons. First, tank C-103 represents the worst case for heavy volatile organic vapors and is the greatest challenge for the development of appropriate sampling and analytical methods. Second, it has unique flammable components in its vapor headspace and has been involved in the majority of the vapor exposure incidents at Hanford. Third, a generic DQO was needed to specifically address "lesser" vapor headspace problems in other storage tanks. Fourth, there are 9 other "organic Watch List tanks" which may have similar headspace constituents but in dramatically lesser concentrations. Fifth, there are 20 FeCN class Watch List tanks which may be potential HCN producers. And lastly, 9 other tanks in BX/BY/C farms have a history of vapor incidents associated with them.

These collective 38 tanks comprise the "Suspect Tank List", which is the primary emphasis of the generic DQO. Additionally, the balance of the 177 Hanford tanks need some degree of signature characterization to determine if they meet "suspect tank criteria." The methods determined to be most successful in tank C-103 will be selected for sampling the other Suspect List tanks covered by the generic vapor DQOs contained in this document.

The DQO process starts by describing the problem. In this case, the generic problems associated with vapors in the tank farms were considered. The DQO process was used to lead the planning team through a structured set of steps that help to describe why data are needed, from where and when should data be collected, how data will be summarized and used in support of a decision, and how much uncertainty in that decision can be tolerated. The products of each step of the process are the generic DQOs. These DQOs will be considered on a tank-by-tank basis and used to develop an appropriate sampling and analysis plan designed to generate the right amount and quality of data for decision making. As better estimates of method performance and spatial and temporal variability of vapor constituents become available, the DQOs will facilitate the statistical design and analysis of all vapor data collection efforts that will take place. By specifying DQOs, an important set of criteria are documented that will enable future data users to determine data adequacy and limitations to support decision making.

The primary expectations of the DQO planning team were to build on the previous DQOs and determine the number and types of samples and analyses needed to resolve vapor safety problems for the other Suspect List tanks, and the tank farms in general. It is expected that these generic vapor DQOs will evolve and change with time. As data becomes available from the pilot project vapor sampling system (VSS) sampling event, as subsequent studies address spatial and temporal variability, and as samples are taken from other Suspect List tanks, a better set of historical data will be generated that may affect understanding of the problem and the types and number of samples needed to address the problem. Prior to each new vapor sampling event, these DQOs will be reviewed by the Vapor Program Manager, and any significant changes will be discussed with the appropriate stakeholders to ensure that whenever possible, data adequate for decision making will be generated by the vapor sampling program.

2.0 DQO STEP 1: STATE THE PROBLEM

2.1 BACKGROUND AND SCOPE

The Tank Vapor Issue Resolution Program was established in 1992 to resolve the health and safety issues related to vapors associated with the high-level waste tanks at the Hanford Site. The issues stem from 1) an insufficient understanding of reported exposures of tank farm personnel to unacceptable levels of noxious vapors; and 2) the concern that until the vapors in the waste tanks are well characterized, the risks to worker health and safety cannot be determined.

High-level radioactive waste generated by processes at the Hanford Site has been stored since the mid-1940s in large underground storage tanks which are grouped into tank farms. Due to the variety of processes at the Hanford Site and the range of waste types stored in the tanks, the history and current inventory of each waste tank are unique.

Nineteen vapor exposure events involving 34 workers at the Hanford Site have occurred between July 1987 and May 1993. During these events, workers have reported ill effects including headaches, burning sensation in nose and throat, nausea, and impaired pulmonary function while working around waste tanks on the Hanford project. Musty and foul odors, including the smell of ammonia, have been reported to emanate from several single-shelled tanks (WHC 1994). Ten of these occurrences, involving 18 workers, were linked to C Tank Farm. In particular, tank C-103 was implicated with six of the reported occurrences.

The scope of this generic vapor characterization effort conducted under the Tank Vapor Issue Resolution Program includes two separate characterization and analytical efforts:

1) In-tank representative characterization or VSS[a] and 2) In-tank signature characterization or in situ sampling (ISS).[a]

In-tank representative characterization involves the headspace vapor sampling process that is evolving at the site, primarily from characterization efforts at tank C-103. This characterization scheme is documented in the Program Plan for the Resolution of Tank Vapor Issues (Osborne 1992). Signature characterization is a characterization program currently under development, and will benefit from the refinement of characterization design based on experience gained through the next few vapor characterization events. As additional information becomes available, the DQO will be updated and revised as needed. As such, this DQO should be viewed as a living document which will evolve with future iterations.

[a] The vapor sample acquisition methods for these two characterization elements are described in Section 7.6.

2.2 PROBLEM STATEMENTS

2.2.1 Flammability Problem

The presence of flammable constituents in the vapors of Hanford waste tanks is a safety question that must be resolved prior to conducting any type of intrusive sampling, stabilization, or remedial activities in or around the tanks. At issue are the potential effects on the tank and the environment should a fire result from these activities. Standard WHC safety practices dictate that the flammability of the headspace of a tank must be measured and determined to be below 20% of the LFL before intrusive work may be conducted on any Watch List tank. Thirty-three of the 39 "suspect tanks" are on Watch List status.

2.2.2 Toxicity Problem

The major health issue which must be resolved is: Are compounds of toxicological significance present in the tanks at such a level that the industrial hygiene group shall be alerted to their presence so adequate breathing zone monitoring can be accomplished and future activities in and around the tanks can be performed in a safe manner.

2.2.3 Approach to Problem Resolution

The tank-by-tank approach to resolving the vapor headspace issues is to first deal with the potentially catastrophic issue of flammability. Until determinations of headspace LFL are determined, a tank cannot be characterized as having a potential flammable or non-flammable problem which will impact operational and sampling practices. Combustible gas meter readings will be taken to determine the % LFL of the headspace vapor. If these readings indicate any potential problem, samples will be taken to determine the composition and concentrations of flammable constituents in the vapor.

With resolution of the flammability issue, appropriate safe operating procedures will be established and headspace vapors will be sampled to characterize potential human health toxicity of the vapors. Dependent upon the identified vapor constituents and their concentrations, the industrial hygiene group will be advised of the presence of compounds of toxicological significance in a tank headspace. With this information in hand, the industrial hygiene group can devise health and safety procedures that will provide worker protection during subsequent sampling and operational activities. This will include personal monitoring to target compounds detected at levels of concern in the tank and to maximize the effectiveness of monitoring the worker breathing zones around the tanks.

2.3 DQO PLANNING PARTICIPANTS

Implementation of the DQO process for vapor health and safety issues involved management and technical staff spanning a wide range of disciplines, including occupational and environmental safety and health experts, engineers, chemists,

statisticians and DQO facilitators. Table 2-1 presents those personnel who participated in each of the four DQO development meetings. [Washington State Department of Ecology (WDOE) was invited to the planning meetings and received meeting notes, but was not in attendance or available for telephone conferences.] Upon completion of this document, comments will be sought by other stakeholders including DOE, USEPA and the WDOE with the goal of obtaining concurrence from all important data users. The major stakeholders have been kept informed in varying degrees about this program, prior to and during the development of these DQOs.

Table 2-1
Invited Participants in the DQO Development Effort

PARTICIPANT	MEETING DATE 12-14-93	01-03-94	01-18-94	02-01-94	Stakeholder Review 02/23/94
WHC:					
J. Osborne, Manager Vapor Program	x	x	x	x	x
J. Huckaby, Engineer		x		x	
T. Rudolph	x				
E. Hewitt	x		x		
P. Morant		x		x	
J. Harbinson		x			
B. Conrad					x
Northwest Instrument Systems:					
M. Story			x	x	x
Hanford Environmental Health Foundation:					
J. Calcagni					x
PNL:					
C. Anderson, Statistician		x	x	x	x
J. Young	x	x	x	x	
D. Mahlum, Toxicologist	x	x	x		
K. Tominey		x	x		
K. Remund, Statistician			x		
B. Pulsipher, Statistician				x	x
P. Turner, DQO Meeting Coordinator	x	x	x		
Neptune and Company:					
D. Michael, DQO Facilitator	x	x	x		x
R. Ryti, DQO Facilitator	x			x	
J. McCann, DQO Facilitator		x	x	x	
DOE-RL:					
S. Branch	x				
P. Hernandez	x				
J. Noble-Dial					x
DOE-GSSC:					
D. Schlick				x	x
WDOE					
M. Lerchen					

3.0 DQO STEPS 2 & 3: IDENTIFY THE DECISIONS TO BE MADE AND INPUTS TO THE DECISION

Two key decisions will be made based on the data collected--a flammability decision and a toxicity decision.

3.1 FLAMMABILITY DECISION

If the flammable gas concentration in the headspace of any tank is greater than 20% of the LFL under steady-state conditions, as measured by the combustible gas meter and/or potential sampling and analysis, then all operational and sampling activity should stop until the problem is investigated and resolved. If the flammable gas concentration in any tank is between 10 and 20% of the LFL in the headspace under steady-state conditions, then work may continue, but a sample will be collected and analyzed to determine the constituents and concentrations of the flammable constituents. If the flammable gas concentration in any tank in less than 10% of the LFL, then operational and sampling work may continue.

3.2 TOXICITY DECISION

If any compounds with toxicological properties exceed their respective trigger points inside the tank, then advise the industrial hygiene group that compounds of toxicological concern are present in the tank headspace. A trigger point is defined as:

- 50% of the appropriate CES concentration for non-carcinogens, and
- 10% of the appropriate CES concentration for carcinogens.

A CES is generally defined as the most stringent of known regulatory or recommended toxicological values for the occupational setting including the threshold limit value (TLV), permissible exposure limit (PEL), recommended exposure limit (REL), and biological exposure limit (BEI). For those constituents with unknown toxicological values, the Toxicology Review Panel (TRP) comprised of toxicologists, industrial hygienists, and occupational medicine physicians will be responsible for development of a CES.

3.3 INPUTS TO THE DECISION

3.3.1 Flammability Decision Inputs

The primary flammability data input will be via combustible gas meter readings, and in some cases, additional determination of the concentration of flammable constituents in the headspace via ISS vapor collection and targeted analysis may be required .

3.3.2 Toxicity Decision Inputs

The following data needs are associated with the toxicity decision:

- Identification of chemical compounds of worker health and safety or toxicological importance in the headspace of the tank.
- Estimates of the concentrations of these toxicologically significant compounds in the headspace.
- Understanding of the toxicological effects of these compounds and the CES for each constituent of concern.

3.3.3 Development of Consensus Exposure Standards

CESs will be generated for each compound of potential toxicological interest detected in the vapor sampling effort. Industrial hygienists have several sources of information for exposure standards against which sampling results may be compared in order to determine whether or not an unacceptable exposure condition exists. A primary source is the American Conference of Governmental Industrial Hygienists (ACGIH) recommended TLVs with some 700 chemicals listed. For compliance purposes, the PELs listed in Subpart Z of the Occupational Safety and Health Administration (OSHA) regulations are used (29 CFR 1910.1000). The National Institute of Occupational Safety and Health (NIOSH) has developed RELs based on recent research and new information about the chemicals, and these RELs are intended for adoption into OSHA regulations. The American Industrial Hygiene Association (AIHA) has also developed Workplace Environmental Exposure Level (WEEL) guides on chemicals for which no current exposure guidelines at the time have been established by other organizations.

In selecting appropriate exposure limits for the chemical constituents in the tank farm headspace vapor, the TRP will first consult the ACGIH TLVs booklet, the OSHA PEL tables, the NIOSH list of RELs, and the AIHA WEELs. The most stringent standard among the above sources will be used.

A chemical may not have published exposure standards. In this case, the TRP can provide a best estimate of the level of acceptable exposure to the chemical. This process for derivation of a consensus exposure limit must rely heavily on professional judgement of the Toxicology Review Panel at Hanford. It may involve an initial literature search in various databases for available information on the chemical. Current data bases may include:

- Registry of Toxic Effects of Chemical Substances (RTECS)
- National Air Toxics Information Clearinghouse (NATICH)
- Integrated Risk Information System (IRIS)
- Gene-Tox Database through the National Library of Medicine
- MEDLINE
- ETIC
- TOXLINE

- CHEMLINE
- Monographs by the International Agency for Research on Cancer (IARC)
- Others as appropriate

Evaluation of health effects may involve a search of information about the chemical or similar analogs on adverse effects, thresholds, possible evidence of carcinogenicity, genotoxicity, developmental toxicity, reproductive toxicity, systemic toxicity, and skin/eye irritation. The no-observable-adverse-effect-level (NOAEL), if available, may be useful for animal-to-human extrapolation. Another numerical value for consideration is the maximum tolerated dose. Generally, factors considered in the toxicity evaluation of a chemical may also include its pharmacokinetic properties, effects on target organs, metabolism (biochemical reaction and transformation), and the rate of absorption and distribution. For example, when considering route-to-route extrapolation, the limitations of extrapolation are clearly apparent and one must account for:

- Difference in absorption efficiency
- Difference in systemic effects
- Occurrence of critical toxic effects at portal of entry
- First-pass effects that may result in either bioactivation or detoxification of a chemical prior to reaching the target organ
- Variations in the time course of target organ concentrations of toxicologically active species

In addition, other factors may include known specific chemical interactions, severity of effects, and other significant effects. The TRP will make various assumptions based on professional judgement to understand toxicological effects for chemicals with little or no known toxicity information. To support the tank farm vapor program, the TRP will apply methods that are scientifically defensible, short of conducting research, to formulate a recommended CES for those chemicals. Insofar as possible, the same approach that AIHA uses in establishing WEELs will be used to evaluate new chemicals.

4.0 DQO STEP 4: DEFINE STUDY BOUNDARIES

Vapor sampling will be eventually conducted on all tanks in the tank farm. This DQO differentiates between 38 of the tanks on the current "Suspect Tank List", tank C-103 (also on the "Suspect Tank List" for which DQOs were developed separately) and all other non-suspect tanks. It further differentiates between those identified as suspect tanks that are actively ventilated, and those that are not.

The spatial boundaries of both the flammability and toxicity decisions for any non-actively ventilated tanks are essentially the internal dimensions of the tank above the level of waste in the tank and not physically inside the dimensions of the riser. This volume is known as the "headspace" of the tank. Due to tank access restrictions that limit access to most of this volume, flammability and toxicity decisions for most tanks will be based on samples taken from a single location at a point approximating the midpoint of the tank volume.

Spatial boundaries for vapor decisions for actively ventilated tanks are the same; however, samples will be collected from the exhaust ventilation headers or stack rather than inside the tanks at some depth below the riser.

Concentrations of constituents in the vapor are not expected to fluctuate greatly over time, and constituents of interest in the vapor are assumed to be homogeneously distributed (well mixed) within the headspace. Accordingly, no effort to consider the time of the year for any tank will be considered. In addition, measurements of vapor constituents from anywhere within the headspace (below the risers) are expected to be representative. If and when results of C-103 samples taken over time and at three depths in the headspace refute these assumptions, the boundaries for the generic vapor DQO will be revisited and the design for sampling will consider these sources of variability.

5.0 DQO STEPS 5: DECISION RULES

The specification of decision rules for each of the identified decisions is a critical step in the DQO process. The decision rule combines the earlier statements into a single statement which specifies how data will be used to make each specified decision. Decision rules for C-103 vapor sampling were adopted for this generic vapor DQO.

5.1 FLAMMABILITY DECISION RULE

The flammability decision rules are stated below. The logic applied to the flammability decision is illustrated in Figure 1.

1. If a single sample of tank vapor fuel content, as measured below the riser with a combustible gas meter (CGM), is greater than 20% of the LFL, then the tank is potentially a flammability hazard and all operational and sampling activity shall cease until the flammability problem is investigated and resolved.

2. If a single sample of tank vapor fuel content, as measured below the riser with a CGM, is 0 to 10% of the LFL, then the tank is not considered a flammability problem and work can proceed.

3. If a single sample of tank vapor fuel content, as measured below the riser with a CGM, is greater than 10% but less than 20% of the LFL, operational and sampling activity may continue under combustible gas monitoring, and sampling will be conducted to determine the vapor constituents and concentrations of the potentially flammable mixture.

Rationale of Decision Rule

The flammability issue for waste storage tanks centers around three potential fuel sources: flammable vapors, flammable floating liquid or interstitial layers and flammable gases (e.g., H_2). This DQO process addresses only the data used to evaluate the flammability of the headspace due to combustible components (i.e., vapors and gases) which may impact the safety of operations. The flammability of a floating liquid or interstitial layer is addressed separately in the Organic USQ DQO document number PNL-8871. Industrial standards for the chemical and gas industries have been adapted for use as guidelines in the Hanford tank farm complex. An additional safety margin has been added to the standard 25% of LFL. The WHC control manual and plant operating procedure level is 20% of LFL. This level is a warning that some condition or process has changed and that some action is needed before operations are continued. The current practice is to measure the LFL and if >20%, then stop work, sample, analyze, and convene the Plant Review Committee (PRC) for review. Their options are to allow continued operation up to some predetermined higher level like 50% LFL or to require dilution or mitigation to reduce the LFL level to below 20% LFL. This logic drives the demand for highly reliable flammability data and a definitive decision rule.

5.2 TOXICITY DECISION RULE

The DQO team established decision rules organizing potentially toxic substances by type to include: the average concentration of any confirmed or suspected human (class A1 or A2) carcinogen, (also teratogens and mutagens), systemic toxins and irritants. The decision rules are specified below. The logic applied to the toxicity decision is illustrated in Figure 2.

1. If the average concentration of any confirmed or suspected human (class A1 or A2) carcinogen, teratogen, or mutagen in a tank headspace is greater than one-tenth of its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

2. If the average concentration of any systemic toxin in a tank headspace is greater than one-half its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

3. If the average concentration of any irritants in a tank headspace is greater than one-half of its CES, then advise the industrial hygiene group that compound(s) of toxicological concern are present in the tank headspace so that appropriate worker protection actions can be taken.

Rational for Decision Rule

For the average concentration of any confirmed or suspected human (class A1 or A2) carcinogens, teratogens and mutagens, a 0.1 safety factor is used in lieu of a 0.5 safety factor for irritants and systemic toxicants. These safety factors are based upon current WHC policy(WHC-CM-4-40). It should be noted that complex mixtures of compounds will be evaluated on a case-by-case basis by the Toxicology Review Panel. Grouping of like compounds and the application of mixture rules will be applied the Toxicology Review Panel to generate combined CESs for toxicity assessments.

5.3 DECISION RULE FOR SIGNATURE CHARACTERIZATION OF NON-SUSPECT LIST TANKS

If any compounds of toxicological interest are identified by the Toxicology Review Panel, then classify the problem as either organic or inorganic (e.g., NH_3, HCN), and collect a more extensive set of samples for representative characterization (see Section 7.6). In general, constituents greater than 10% of their CES will trigger this action. In addition, the Toxicity Review Panel will evaluate the potential adverse effects of complex mixtures as described above, and may request additional samples as appropriate.

FIGURE 1
FLAMMABILITY DECISION LOGIC DIAGRAM

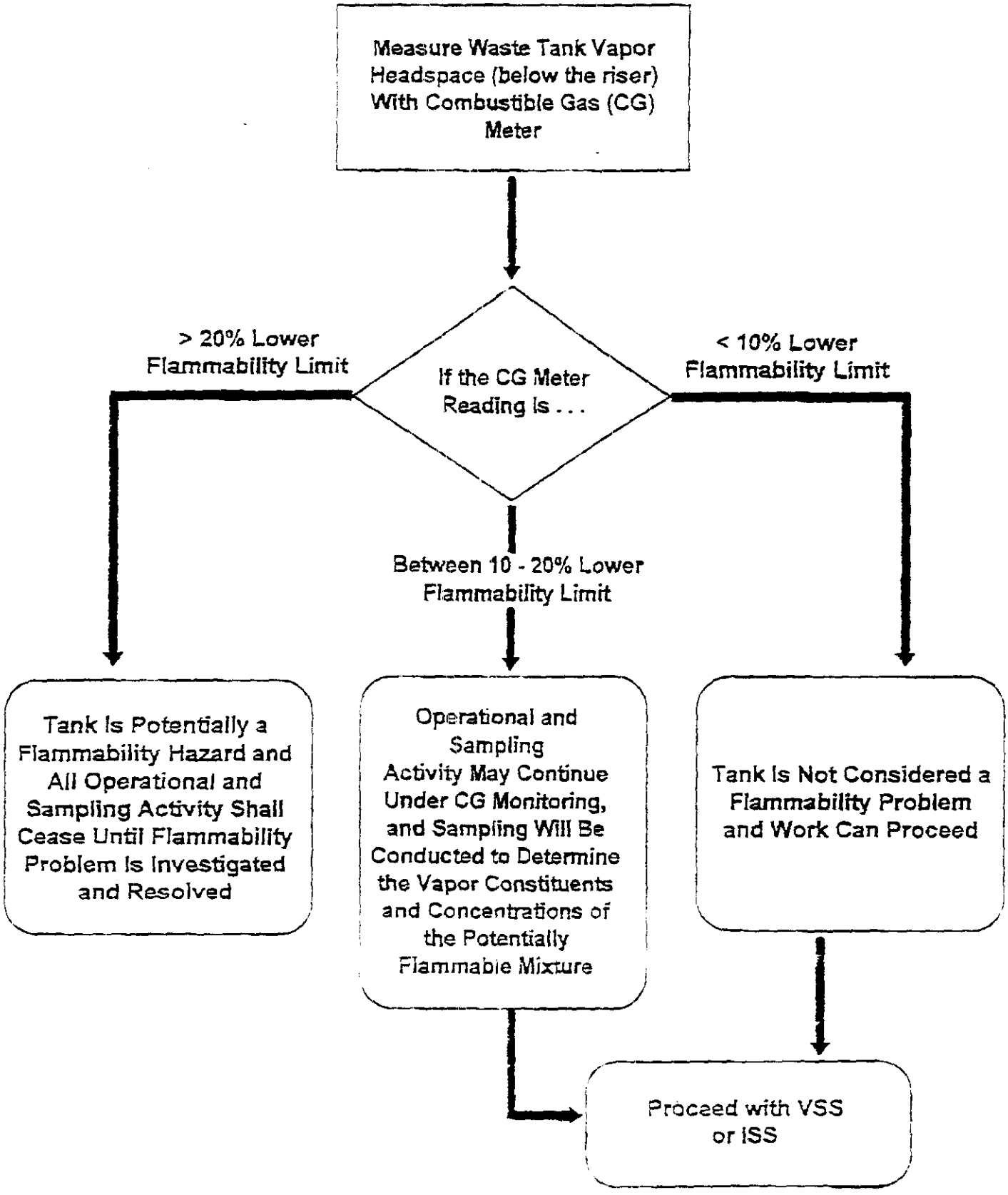
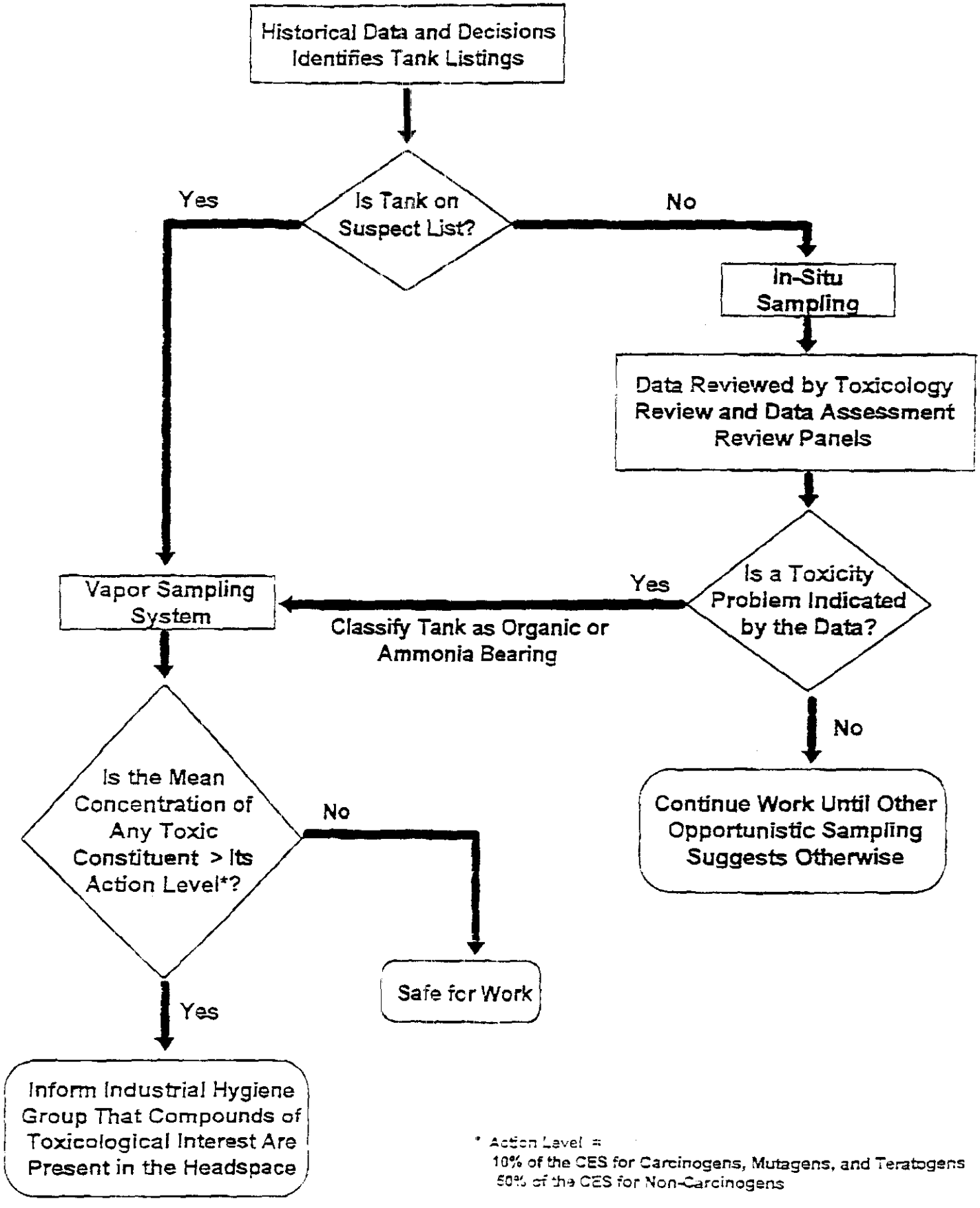


FIGURE 2

TOXICITY DECISION LOGIC DIAGRAM



* Action Level =
10% of the CES for Carcinogens, Mutagens, and Teratogens
50% of the CES for Non-Carcinogens

6.0 DQO STEP 6: LIMITS ON DECISION ERRORS

Limits on decision errors were elicited to provide a criteria against which to measure the expected performance of alternative designs. The DQO planning team decided that the decision errors and corresponding tolerances developed for the tank C-103 DQO effort should apply to the rest of the "Suspect" List tanks. No attempt to specify limits on decision errors for signature characterization events was made by the planning team.

6.1 DEVELOPMENT OF FLAMMABILITY DECISION ERROR LIMITS

The process of specifying limits on decision errors begins by identifying each type of potential decision error and discussing the consequences associated with these error types.

One type of decision error would occur if data indicate that the observed $LFL_{MIX} \geq 20\%$ (flammability is a concern), when the "true" LFL_{MIX} is < 20% (as determined by additional vapor sampling for any reason). If this occurs, work will be stopped, a safety review will be implemented unnecessarily, and a more complex analysis of LFL will be conducted. These actions would result in the following consequences:

- Increased costs
- Schedule delays
- Possible negative impact on critical path
- Credibility loss.

A second kind of decision error would occur if data indicate that the observed $LFL_{MIX} < 20\%$ (no concern with flammability), when the "true" LFL_{MIX} is $\geq 20\%$. If this occurs, then additional sampling will proceed with sampling methods that could introduce ignition sources to the headspace.

This decision error is of MAJOR CONCERN and has the following consequences:

- Potential negative safety implications
- Increased costs
- Credibility loss (when the correct....)
- Possible continued use of unacceptable operating techniques.

Desired Performance Curve Inputs

After identifying the decision errors and their associated consequences, the planning team considered a series of potential error scenarios (presumed true LFL values) and specified their aversion to these specific potential decision errors in a desired performance (Table 6-1).

Table 6-1
Desired Performance for the Flammability Decision

Presumed true fraction of the LFL	Acceptable probability of deciding to stop work
less than 0.15	≤10%
0.15 to 0.20	-
0.20 to 0.50	≥90%
more than 0.50	≥99%

6.2 DEVELOPMENT OF TOXICITY DECISION ERROR LIMITS

One type of decision error would occur if we observe that the action level (10% of the CES for carcinogens, and 50% of the CES for systemic toxicants and irritants) has been exceeded, when, in fact, the "true action level" has not been exceeded. If this decision error occurs, then worker protection control measures and breathing zone monitoring requirements will be over-prescribed, resulting in the following consequences:

- Increased costs
- Injury or illness to workers resulting from the wearing of personal protection equipment
- Credibility loss
- Scheduled delays.

A second type of decision error would occur if we observe that the action level (10% of the CES for carcinogens, and 50% of the CES for systemic toxicants and irritants) has not been exceeded, when in fact the "true action level" has been exceeded. If this decision error occurs, then workers could potentially be exposed to toxic vapors. This decision error is of major concern and would result in the following consequences:

- Potential worker illness
- Credibility loss
- Increased costs
- Liability to WHC/DOE.

Desired Performance Curve Inputs

Three different sets of constituents were considered independently due to the types of consequences and differences in action levels. Tables 6-2, 6-3, and 6-4 depict the decision error limits established during the DQO development exercise. Since the consequences were most severe for carcinogens, the error tolerances were tightest for these constituents. In all likelihood, these constraints will drive the sampling and analysis design. In fact, the analytical experts predicted that a design adequate to determine if benzene exceeded its CES would be more than adequate to make decisions for all other constituents of concern.

Table 6-2
Desired Performance for the Toxicity Decision:
Average Concentration of Confirmed/Suspected Human (Class A1/A2)
Carcinogenic, Teratogenic or Mutagenic Constituents

Presumed "true" fraction of the CES	Acceptable probability of deciding toxic constituents are present
less than 0.01	≤1%
0.01 to 0.05	≤20%
0.05 to 0.1	-
0.1 to 0.5	≥80%
0.5 to 1	≥95%
1 or more	≥99%

Table 6-3
Desired Performance for the Toxicity Decision:
Systemic Toxicant Constituents

Presumed "true" fraction of the CES	Acceptable probability of deciding toxic constituents are present
less than 0.05	≤1%
0.05 to 0.25	≤25%
0.25 to 0.5	-
0.5 to 1	≥95%
more than 1	≥99%

Table 6-4
Desired Performance for the Toxicity Decision: Irritant Constituents

Presumed "true" fraction of the CES	Acceptable probability of deciding toxic constituents are present
less than 0.05	≤1%
0.05 to 0.25	≤25%
0.25 to 0.5	-
0.5 to 1	≥95%
1 or more	≥99%

7.0 SAMPLING AND ANALYSIS DESIGNS FOR OBTAINING DATA

7.1 STATISTICAL TERMINOLOGY

The performance tables in Section 6 provide a tool for the decision makers to describe the acceptable probability of making a decision error. The theory behind these tables is based on statistical hypothesis testing, in which the data are used to decide between one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternative hypothesis, H_A). The null hypothesis is assumed to be true in the absence of strong evidence to the contrary. A decision error occurs when the decision makers are led to believe in one hypothesis when the other is true.

There are two types of decision errors that must be considered. The first type of decision error occurs when the decision makers conclude, based on the data, that H_A is true when, in fact, H_0 is true. This error is sometimes referred to as a false positive, or a Type I, error. When the decision makers specify how often they can tolerate making this type of decision error (e.g. 5 out of 100 times), that is often referred to at the Type I error rate, or α. The second error occurs when the decision makers conclude, based on available data, that H_0 is true when, in fact, H_A is true. This error is sometimes referred to as false negative, or Type II, error. The Type II error rate, or β, is the specification of how often the decision maker can tolerate making this type of decision error.

7.2 DESIGN ASSUMPTIONS

For each vapor sampling event, the flammability and toxicity decision rule will both be addressed. The two assumptions of importance are that the headspace is anticipated to be relatively homogeneous, and that the total study error is approximately equal to measurement error.

7.3 SELECT THE APPROPRIATE STATISTICAL TEST

The hypotheses and statistical tests developed for C-103 heated tube flammability determinations are applicable for generic vapor flammability determinations that are based on the analysis of flammable constituents. For most tanks, the expected value of the CMG is expected to be well below 10% of the LFL. In these cases, a direct comparison of the measured value to 10% of the LFL will be used; hence no statistical test will be conducted.

The hypotheses for the toxicity decision rule for carcinogens are distinguished by a comparison of the average concentrations of confirmed or suspected human (class A1 or A2), carcinogens (this includes teratogens and mutagens) to their corresponding action level (0.1 times the CES for carcinogens). The goal of the testing procedure is to determine if there is sufficient evidence in the collected data to reject the hypothesis that the average concentration of carcinogens is greater than the action level. The

appropriate classical statistical test for resolving this problem is a one sided t-test. The hypotheses can be stated as follows:

H_0: Mean concentration of each carcinogen $\geq$ 0.1 times CES

H_A: Mean concentration of each carcinogen < 0.1 times CES.

The desired performance (Table 6-2) indicates that the specified probability of deciding toxic constituents are present at the hypothesis boundary of 0.1 times CES is 0.80. Since this corresponds to making the correct decision when the null hypothesis is true, the probability of making an incorrect decision when the null hypothesis is true (i.e., the probability of deciding H_A when in fact H_0 is true) is one minus 0.80, or 0.20. Thus, the Type I error rate, or α, is 0.20 (i.e., the probability of deciding that toxic constituents are not present when, in fact, they are, is no greater than 0.20). Also indicated is that the probability of deciding to stop work at 0.05 times the CES should be $\leq$ to 0.20. Since this corresponds to making an incorrect decision when the alternative hypothesis is true, the Type II error rate at 0.05 times CES, or β at 0.05 times CES, is 0.20 (i.e., the probability of deciding that the toxic constituents are present when, in fact, they are not, is no greater than 0.20). The region of decision indifference is defined in the desired performance curve at 0.05 to 0.10 times CES.

The hypotheses for the toxicity decision rule for systemic toxins and for irritants are distinguished by a comparison of the average concentrations of systemic toxins or irritants to the action level of 0.5 times its CES. The appropriate classical statistical test for resolving these problems is a one sided t-test. The hypotheses can be stated as follows:

H_0: Mean concentration of each systemic toxin $\geq$ 0.50 x CES

H_A: Mean concentration of each systemic toxin < 0.50 x CES

and

H_0: Mean concentration of each irritant $\geq$ 0.50 x CES

H_A: Mean concentration of each irritant < 0.50 x CES.

The desired performance curves for these decisions are found in Tables 6-3 and 6-4. Using the same discussion as for carcinogens, the Type I error rate, or α, for these constituents is 0.05. The Type II error rate at 0.25 times CES, is 0.25. The region of decision indifference is between 0.25 and 0.5 times CES.

7.4 OBTAIN PERTINENT ESTIMATES OF UNCERTAINTY

No estimates of uncertainty were available for the measurement error for the $FC_{Mixture}$. As data appropriate for obtaining pertinent estimates of uncertainty become available from C-103, statistical sampling designs will be

considered for other Suspect List tanks. Until that time, professional engineering based designs will be used to obtain samples for decision making.

Estimates of uncertainty for the toxicity decision rule also do not exist at this time. Engineering judgement estimates of the important sources of uncertainty could be obtained, but none of the estimates can be directly tied to observed data.

7.5 POWER ANALYSIS

No power analyses were performed for either the flammability or toxicity decision rules because no prior estimates of uncertainty were available. A retrospective power analysis could provide a useful look at the achievable probabilities of decision error as estimates of uncertainty become available.

7.6 VAPOR SAMPLE ACQUISITION METHODS

Two methods will be used to collect gas and vapor samples for the waste tanks. The primary method employs heated transfer tubing, a heated sampling manifold, relatively sophisticated temperature, flow control, and valving technology, and a vacuum pump to draw air, gases, and vapors out of the waste tanks. Different types of samples can be taken from several stations of the manifold, which is housed with the measurement and control equipment in a climate-controlled mobile laboratory. This method currently requires that a special vapor sampling probe be installed by crane into a riser of the tank. The integrated equipment (e.g., probe, heated transfer tubing, and everything in the mobile laboratory) is referred to as the Vapor Sampling System or VSS.

The VSS was specifically designed to collect representative samples from warm, moist tanks, even if there is a fog in the headspace. Advantages of the VSS include the abilities to perform sampling in adverse weather conditions, to house real-time analytical equipment, and to address high concentrations of organic vapors. Problems yet to be fully addressed include the potential adsorption and loss of certain species on the walls of the transfer lines, and the limitations of a single system to meet the desired sampling schedule.

The second method for collecting gas and vapor samples from the waste tanks is referred to as ISS. Rather than transferring the air, gases, and vapors to be sampled to a remote location, the sampling devices themselves (specifically sorbent traps) are lowered down into the headspace of the tank. This assures representative samples and avoids problems associated with the loss of analytes via wall adsorption.

The ISS method uses simple, inexpensive flow monitoring and control equipment, which currently is mounted on a 2-wheel hand cart. The required equipment is easy to maintain and duplicate. The ISS method provides the ability to collect samples quickly and without the special sampling probe of the VSS. Disadvantages of the ISS method include current limitations on its ability to sample some volatile organic vapors under certain conditions (e.g., acetone in a high-humidity tank) and that each sampling event involves breaking the

containment of the tank. The shipment and analysis of ISS sorbent traps is also currently dependent on proving no radiolytic contamination of the traps has occurred.

A limited ISS event that addresses the most significant noxious gases and vapors, requiring less than 1 hour at an open tank riser, is planned for each single-shell waste tank scheduled for intrusive work, on an opportunistic basis. The opportunistic use of the ISS method is being designed to maximize information obtained while minimizing sampling costs and time. These sampling events are currently designed to collect triplicate sorbent trap samples of ammonia, nitrogen dioxide, nitrogen monoxide, and water vapor. Additionally, triplicate SUMMA canister samples will be collected from the same vicinity as the other samples via an unheated tube, and will be analyzed for volatile organic vapors. Potential radiolytic contamination of the sorbent traps will be addressed by simultaneously collecting a OVS trap for sacrificial radiolytic analysis. The ISS method will also be used to examine several waste tanks for the presence of hydrogen cyanide gas, in support of the Ferrocyanide Tank Safety Program.

7.7 ADAPTIVE ANALYSIS STRATEGY

For the generic tank vapor analysis, the following adaptive analysis strategy will be employed.

If a pre-existing flammable safety concern is relevant, a flammability meter reading and/or an in situ sorbent sampling using OSHA Versatile Sampling and analysis technology as described in "Aerosol and Vapor Characterization of Tank 241-C-103" (PNL-8875/UC-606) or equivalent will be employed for resolution.

If not, a representative sample of the tank headspace will be taken in a manner that has been shown to be effective to address any documented concerns and the DQOs for that tank, (SUMMA canisters, sorbent tubes, impingers). Standard, accepted, ambient air analysis methodologies such as chemical class detectors (hydrocarbon, halogen, etc.), gas chromatography, mass spectrometry, ion chromatography or colorimetry will be employed to determine concentrations above 1 part per billion (volume). The analysis will specify by chemical the concentration detected and the confidence of that measurement. Historically achieved performance can be substituted for non-standard gases. If the list of identified gases contains any analytes that are of concern to the program; e.g., toxicity, those concerns will be judged with respect to the data and a determination made as to the adequacy of the sampling and analysis or whether additional work needs to be done. This may mean the convening of an expert panel, operational controls or other resolution means that are cost effective.

This methodology is being employed with respect to tank C-103, and the anticipated dates for accomplishment are:

Representative sampling	January 27, 1994
List of analytes present	February 23, 1994
Identification of analytes of concern	March 1, 1994
Selection of analytical method(s)	March 9, 1994
Modification of methods	June 30, 1994
Quantitative analysis to a known certainty	June 30, 1994

8.0 REFERENCES

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